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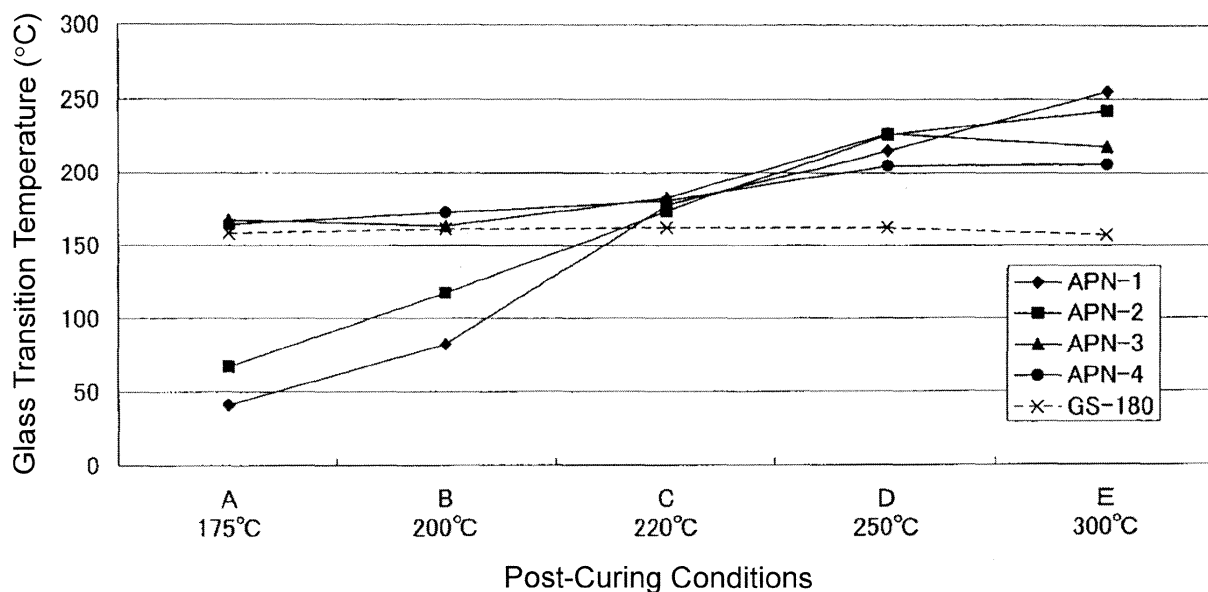
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(54) **Method for manufacturing cured product of thermosetting resin composition and cured product obtained thereby**

(57) The present invention relates to a method for producing a cured product of a thermosetting resin composition, the method including: heating a thermosetting resin composition including the following ingredients (A) to (C) at a temperature of 100 to 200°C for 1 to 60 minutes;

and then further heating the thermosetting resin composition at a temperature of 220 to 350°C for 10 to 6,000 minutes, thereby curing the thermosetting resin composition: (A) an allyletherified phenol resin; (B) an epoxy resin; and (C) a curing accelerator.

Fig. 1



Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method for producing a cured product of a thermosetting resin composition which is used for an encapsulating material requiring high heat resistance in a power device or the like and is excellent in long-term heat resistance and heat cycle resistance, and a cured product obtained thereby.

BACKGROUND OF THE INVENTION

[0002] Usually, semiconductor devices have hitherto been fabricated by encapsulating semiconductor elements such as transistors, ICs and LSIs with ceramic packages, plastic packages or the like. The former ceramic packages have excellent durability under high temperature and high humidity, because their constituent materials themselves have heat resistance and also have excellent humidity resistance, and further have excellent mechanical strength. Accordingly, highly reliable encapsulation is possible. However, the above ceramic packages have problems that the constituent materials are relatively expensive and that the packages are poor in mass productivity. In recent years, therefore, resin encapsulation with the latter plastic packages has become mainstream. In the resin encapsulation with the above plastic packages, epoxy resin compositions have hitherto been used by utilizing their property of excellent heat resistance, and achieve satisfactory results. As such an epoxy resin composition for encapsulating the semiconductor elements, there has been generally used a composition including an epoxy resin as a main material, a phenol resin as a curing agent, an amine-based compound as a curing accelerator, and other optional ingredients such as a rubber ingredient as an elasticity imparting agent and a silica powder as an inorganic filler, particularly as a composition excellent in terms of encapsulating workability and the like at the time of transfer molding.

[0003] On the other hand, some insulating materials such as a semiconductor encapsulating material including an allyl group-containing phenol resin have hitherto been proposed. However, the actual situation is that no material sufficiently satisfying heat resistance is obtained yet. The above insulating materials such as a semiconductor encapsulating material including an allyl group-containing phenol resin include, for example, one intending to improve adhesiveness (see Patent Document 1), one improving moisture absorption resistance (see Patent Document 2), one decreasing the melt viscosity of a thermosetting resin composition (see Patent Document 3), one intending to improve laser marking properties (see Patent Document 4), one having low-temperature expansion (see Patent Document 5) and the like. These are satisfactory in respective characteristics, but do not sufficiently satisfy heat resistance. Further, as an example of improving heat resistance, there is proposed a thermosetting resin composition including an allyl group-containing phenol resin and a bismaleimide resin (see Patent Document 6). However, the reactivity of the bismaleimide resin-containing thermosetting resin composition is poor, compared to an epoxy resin-phenol resin curing reaction which is generally used in the encapsulating materials and the like at the time of molding, and has a problem of poor workability. Furthermore, there are ones improving the glass transition temperature by using thermosetting resin compositions each including an allyl group-containing phenol resin and a epoxy resin (see Patent Documents 7 to 10). However, the post-curing temperature of these is 200°C or less in all cases, so that the above allyl group is not cured, not leading to improvement in heat resistance. The allyl group requires a high temperature exceeding 200°C for thermal curing and is very low in reactivity. Accordingly, the actual situation is that it has not been studied to improve heat resistance by positively curing the allyl group.

[0004] Patent Document 1: JP-A-8-306828

Patent Document 2: JP-A-7-145300

Patent Document 3: JP-A-9-31167

Patent Document 4: JP-A-4-249526

Patent Document 5: JP-A-6-263841

Patent Document 6: JP-A-3-237126

Patent Document 7: JP-A-2001-11161

Patent Document 8: JP-A-5-132539

Patent Document 9: JP-A-5-320317

Patent Document 10: JP-A-6-136093

SUMMARY OF THE INVENTION

[0005] By the way, power devices such as transistors, diodes and thyristors are used as semiconductor devices for performing high power control or the like in major appliances or industrial instruments. In such power devices, replacement of Si elements to SiC elements or GaN elements has been studied, in order to substantially decrease the loss in electric power converters. It becomes possible to increase the capacity by the replacement to the SiC elements or the GaN

elements. As a result, it is considered that the semiconductor elements are exposed to high voltage to cause an exothermic temperature thereof as extremely high as 200 to 250°C. There is therefore a possibility that when the semiconductor elements have poor heat resistance, breakage of the packages or the semiconductor elements becomes liable to occur.

[0006] As a method for improving heat resistance of the encapsulating resin, it is also considered to add silicone oil or a rubber ingredient into the encapsulating resin composition. However, there is a concern that these additive ingredients seep into an interface between a frame and the encapsulating resin to pose a problem of decreasing adhesive force in the interface.

[0007] On the other hand, as molding methods for encapsulating semiconductor elements, there are various molding methods such as screen printing or dispense molding using a liquid encapsulating resin, and transfer molding, sheet molding or compression molding using a solid encapsulating resin. In each case where the molding methods are used, fluidity and curability are required for thermosetting resin compositions.

[0008] Among the thermosetting resin compositions, there are also high heat-resistant thermosetting resin compositions. However, it is considered that such thermosetting resin compositions are deteriorated in formability by poor curability due to a slow reaction rate thereof. Further, some thermosetting resin compositions produce by-products such as gas at the time of thermal curing reaction. In the case where such thermosetting resin compositions are used for semiconductor encapsulating material applications, when the by-products such as gas are produced during molding, voids and the like are formed in the encapsulating resins caused by the gas, which poses a problem of decreasing reliability, such as the occurrence of failures of devices.

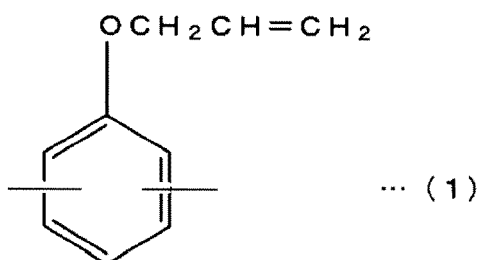
[0009] The invention has been made in view of such a situation, and an object thereof is to provide a method for producing a cured product of a thermosetting resin composition having high heat resistance, which has high glass transition temperature, is excellent in long-term heat resistance and can improve reliability as a device, for example, in insulating applications in electronic parts requiring high heat resistance, such as a power device; and a cured product obtained thereby.

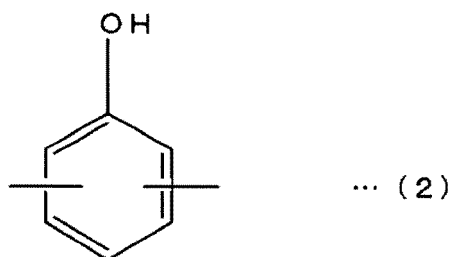
[0010] Namely, the present invention relates to the following items 1 to 5.

1. A method for producing a cured product of a thermosetting resin composition, the method including: heating a thermosetting resin composition including the following ingredients (A) to (C) at a temperature of 100 to 200°C for 1 to 60 minutes; and then further heating the thermosetting resin composition at a temperature of 220 to 350°C for 10 to 6,000 minutes, thereby curing the thermosetting resin composition:

- (A) an allyletherified phenol resin;
- (B) an epoxy resin; and
- (C) a curing accelerator.

2. The method for producing a cured product of a thermosetting resin composition according to item 1, in which the allyletherified phenol resin as ingredient (A) contains the following structural units (1) and (2):





15 3. The method for producing a cured product of a thermosetting resin composition according to item 1 or 2, in which the allyletherified phenol resin as ingredient (A) has an allyl group equivalent of 100 to 3,000 (g/eq.).

4. The method for producing a cured product of a thermosetting resin composition according to any one of items 1 to 3, in which the allyletherified phenol resin as ingredient (A) has a phenolic hydroxyl group equivalent of 100 to 3,000 (g/eq.).

20 **[0011]** 5. A cured product obtained by the method for producing a cured product of a thermosetting resin composition according to any one of items to 4.

25 **[0012]** The present inventors have made intensive studies in order to solve the above problems. As a result, when the cured product is prepared by using the thermosetting resin composition containing the above allyletherified phenol resin (ingredient (A)), the epoxy resin (ingredient (B)) and the curing accelerator (ingredient (C)), first heating this composition at a temperature of 100 to 200°C for 1 to 60 minutes, and thereafter heating it at a temperature of 220 to 350°C for 10 to 6,000 minutes, it has been found that the resulting cured product can sufficiently satisfy long-term heat resistance of, for example, 200 to 250°C or more, and can be used for applications requiring high heat resistance, such as a power device. Thus, the invention has been reached.

30 **[0013]** The above allyletherified phenol resin (ingredient (A)) has phenolic hydroxyl groups, and the epoxy resin (ingredient (B)) has epoxy groups. Accordingly, it is considered that release of the thermally cured thermosetting resin composition from a mold becomes easy by reacting them by heating at a temperature of 100 to 200°C described above to improve productivity in a resin encapsulation molding process using a semiconductor encapsulating material, which is represented by transfer molding. Further, the above allyletherified phenol resin (ingredient (A)) can be post-cured under a temperature condition of 220°C or more, because it has allyl groups. That is to say, it is considered that when a part of the allyl groups are thermally cured under a temperature condition of 220°C or more, the glass transition temperature (T_g) of the cured product is improved. Further, when crosslinked portions formed by the epoxy groups and the phenolic hydroxyl groups are cleaved, for example, by exposure to an extremely high use environment temperature of the power device, there is a concern that the cured product of the thermosetting resin composition becomes soft. However, the allyl groups of the allyletherified phenol resin (ingredient (A)), which do not take part in the above curing, are presumed to gradually react by high temperature to form strong bonds.

35 **[0014]** Then, the present inventors have made a series of studies, and as a result, have found that the cured product obtained using the thermosetting resin composition including the above ingredient (A), ingredient (B) and ingredient (C) under the above specific heat curing conditions can sufficiently satisfy long-term heat resistance at a temperature of 200 to 250°C or more and can be used for applications requiring high heat resistance, such as the power device.

40 **[0015]** As described above, the invention relates to a method for curing the above thermosetting resin composition by using the thermosetting resin composition including the above allyletherified phenol resin (ingredient (A)), the epoxy resin (ingredient (B)) and the curing accelerator (ingredient (C)), heating this composition at a temperature of 100 to 200°C for 1 to 60 minutes, and further heating it at a temperature of 220 to 350°C for 10 to 6,000 minutes. The cured product thus obtained can be subjected to screen printing or dispense molding using a liquid encapsulating resin, or transfer molding, sheet molding, compression molding or the like to form a semiconductor device. The resulting semiconductor device is difficult to be decomposed even when exposed under a high-temperature atmosphere such as 200 to 250°C for a long period of time. Thus, excellent long-term heat resistance is imparted thereto.

45 **[0016]** Then, when the allyl group equivalent of the above allyletherified phenol resin (ingredient (A)) is from 100 to 3,000 (g/eq.), the cured product having more excellent heat resistance is obtained.

50 **[0017]** Further, when the phenolic hydroxy group equivalent of the above allyletherified phenol resin (ingredient (A)) is from 100 to 3,000 (g/eq.), the cured product having more excellent heat resistance and curability is obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

Fig. 1 is a post-curing conditions-glass transition temperature (°C) curve graph showing changes in glass transition temperature depending on post-curing conditions of cured products of allyletherified phenol resins or a phenol resin and an epoxy resin (EPPN-501HY, manufactured by Nippon Kayaku Co., Ltd., epoxy equivalent: 169 g/eq.).

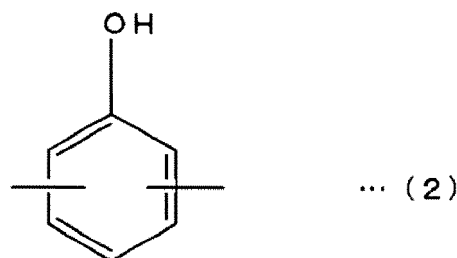
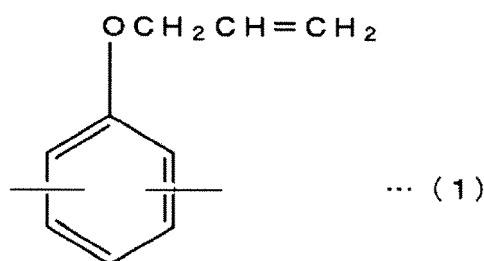
Fig. 2 is a post-curing conditions-glass transition temperature (°C) curve graph showing changes in glass transition temperature depending on post-curing conditions of cured products of allyletherified phenol resins or a phenol resin and an epoxy resin (KI-3000, manufactured by Tohto Kasei Co., Ltd., epoxy equivalent: 200 g/eq.).

DETAILED DESCRIPTION OF THE INVENTION

[0019] The thermosetting resin composition used in the invention is obtained using an allyletherified phenol resin (ingredient (A)), an epoxy resin (ingredient (B)) and a curing accelerator (ingredient (C)), and usually served as an encapsulating material in the form of liquid, powder or a tablet formed through tableting from the powder.

[0020] The above allyletherified phenol resin (ingredient (A)) is, for example, a phenol resin having the following structural unit (1) and structural unit (2):

[0021]



[0022] The phenolic hydroxyl group equivalent (phenol number) of the above allyletherified phenol resin (ingredient (A)) is preferably in the range of 100 to 3,000 (g/eq.), more preferably from 100 to 1,000 (g/eq.), and particularly preferably from 100 to 500 (g/eq.). The reasons for this are as follows. In the case where the phenolic hydroxyl group equivalent is too small, there is a tendency that the breaking elongation is difficult to increase, which may be caused by increased density of crosslinked points of the cured product. On the other hand, in the case where the phenolic hydroxyl group equivalent is too large, there is a tendency that curability decreases.

[0023] Further, the allyl group equivalent (allyl number) of the above allyletherified phenol resin (ingredient (A)) is preferably in the range of 100 to 3,000 (g/eq.), more preferably in the range of 100 to 2,000 (g/eq.), and particularly preferably in the range of 100 to 1,000 (g/eq.). The reasons for this are as follows. In the case where the above allyl group equivalent is too small departing from the above range, there is a tendency that the breaking elongation is unfavorably difficult to increase, which may be caused by increased density of crosslinked points of the cured product obtained. On the other hand, in the case where the above allyl group equivalent is too large departing from the above range, there is a tendency that heat resistance deteriorates.

[0024] The above allyletherified phenol resin (ingredient (A)) can be synthesized, for example, in the following manner. That is to say, the desired allyletherified phenol resin can be obtained by mixing a phenol resin and an allyl halide in a solvent under basic conditions, and stirring them under heating. Further, the desired allyletherified phenol resin can also be similarly synthesized by mixing and polymerizing a previously allyletherified compound which forms a monomer unit of a phenol resin and formalin. The allyletherified phenol resin thus synthesized is a phenol resin containing the above structural units (1) and (2), as described above.

[0025] The above allyletherified phenol resins (ingredient (A)) include, for example, phenol-novolac type, triphenylmethane type, diphenylmethane type and furan ring-containing dicyclopentadiene-novolac type phenol resins. These may be used either alone or as a combination of two or more thereof.

[0026] As the epoxy resin (ingredient (B)) used in combination with the above ingredient (A), a multifunctional epoxy resin is preferably used. Examples thereof include phenol-novolac type, cresol-novolac type, triphenylmethane type, diphenylmethane type and furan ring-containing dicyclopentadiene-novolac type epoxy resins. These may be used either alone or as a combination of two or more thereof.

[0027] The epoxy equivalent (epoxy number) of the above epoxy resin (ingredient (B)) is preferably in the range of 100 to 3,000 (g/eq.), more preferably in the range of 100 to 1,000 (g/eq.), and particularly preferably in the range of 100 to 500 (g/eq.). That is to say, in the case where the above epoxy equivalent is too small departing from the above range, there is a tendency that the breaking elongation is unfavorably difficult to increase, which may be caused by increased density of crosslinked points of the cured product. On the other hand, in the case where the epoxy equivalent is too large departing from the above range, there is a tendency that curability deteriorates.

[0028] For the compounding ratio of the above allyletherified phenol resin (ingredient (A)) and the epoxy resin (ingredient (B)), the epoxy equivalent of the ingredient (B) is preferably set to the range of 0.5 to 3.0 equivalents based on equivalent of the phenolic hydroxyl groups of the ingredient (B), from the viewpoint of reactivity thereof. Then, from the viewpoint of the above reactivity, the epoxy equivalent of the ingredient (B) is more preferably set to the range of 0.6 to 2.0 equivalents, and particularly preferably to the range of 0.8 to 1.5 equivalents.

[0029] The curing accelerators (ingredient (C)) used in combination with the above ingredient (A) and ingredient (B) include, for example, amine-based curing accelerators, imidazole-based curing accelerators, organophosphorus curing accelerators, boron-based curing accelerators, phosphorus-boron-based curing accelerators and the like. These may be used either alone or as a combination of two or more thereof. Above all, organophosphorus curing accelerators and imidazole-based curing accelerators are preferably used in terms of general versatility in the market and cost.

[0030] The content of the above curing accelerator (ingredient (C)) is preferably in the range of 0.01 to 10% by weight based on the total content of the above ingredient (A) and ingredient (B), and more preferably in the range of 0.05 to 5% by weight. The reasons for this are as follows. In the case where the content of the above curing accelerator (ingredient (C)) is too small departing from the above range, there is a tendency that curability deteriorates. On the other hand, in the case where the content of the above curing accelerator (ingredient (C)) is too large departing from the above range, there is a tendency of leading to deterioration of electric characteristics or a decrease in heat resistance.

[0031] The thermosetting resin composition according to the invention may suitably contain a catalyst, a filler, a reinforcing material, a flame retardant, a releasing agent, a coupling agent, a plasticizer, a curing assistant, a coloring agent, a flexibilizing agent, a solvent or the like, in addition to the above ingredients (A) to (C), as needed, within the range not impairing the effects of the invention.

[0032] The cured product obtained by the method for producing a cured product of a thermosetting resin composition according to the invention contains the allyletherified phenol resin (ingredient (A)), so that it is a cured product in which the allyl groups are positively cured. As described above, in the curing reaction of the thermosetting resin composition containing the allyletherified phenol resin (ingredient (A)), the epoxy resin (ingredient (B)) and the curing accelerator (ingredient (C)), a curing reaction due to epoxy-phenol curing occurs by heating at 100 to 200°C as a first-stage reaction process, and the allyl groups having resistance to pyrolysis are cured by heating at 220 to 350°C as a second-stage reaction process, thereby obtaining the cured product. In the invention, pyrolysis of the cured product is inhibited by the curing reaction of the allyl groups to realize improvement in glass transition temperature. For example, when the allyletherified phenol resin in which the Claisen rearrangement has partially proceeded is heated under conditions of 200°C for 100 hours, the Claisen rearrangement proceeds in allylether group moieties, and the allyl group is rearranged to at least one of the ortho- and para-positions of the phenolic hydroxyl group. However, no curing reaction proceeds at all.

[0033] When the cured product is prepared by the method for producing a cured product of a thermosetting resin composition according to the invention, it is necessary to conduct the reaction at a temperature of 100 to 200°C, preferably at a temperature of 150 to 200°C, in order to perform pre-curing, in view of moldability in transfer molding, sheet molding, compression molding, screen printing, dispense molding and the like. Further, the reaction time at the above temperature is from 1 to 60 minutes, more preferably from 1 to 30 minutes, and particularly preferably from 1 to 10 minutes. Further, in order to accelerate the curing reaction of the allyl groups, after the reaction is conducted under the above conditions, heating is performed at 220 to 350°C for 10 to 6,000 minutes, particularly preferably at 220 to 300°C for 10 to 1,440 minutes, thereby inhibiting pyrolysis, which makes it possible to obtain the cured product having high glass transition

temperature. In the case where the above temperature is too low departing from the above range, it becomes difficult that the allyl groups sufficiently react, so that there is a concern that improvement in heat resistance and glass transition temperature is adversely affected. This is therefore unfavorable. On the other hand, the above-temperature is too high departing from the above range, there is a concern that pyrolysis of the cured product leads to deterioration of heat resistance.

[0034] Further, even when a crosslinked structure of the cured product obtained by curing the thermosetting resin composition under long-term high temperature conditions is partially severed by allowing the curing reaction to gradually proceed under a use environment of a semiconductor device at high temperature (for example, 200 to 250°C), the above allyl groups repair the crosslinked structure to impart long-term heat resistance. As for the pyrolysis of the above cured product, for example, the weight loss is preferably 10% by weight or less, more preferably 7.5% by weight or less and still more preferably 5% by weight or less, under conditions of 250°C for 1,000 hours. That is to say, in the case where the weight loss by the pyrolysis of the above cured product is too large departing from the above range, there is a concern that it causes the occurrence of cracks or voids to lead to a failure of the semiconductor device, for example, when the cured product is used as a semiconductor encapsulating material. Incidentally, the weight loss in the pyrolysis of the above cured product is measured and calculated, for example, in the following manner. That is to say, a predetermined amount of the thermosetting resin composition is prepared, cured by heating at 175°C for 5 minutes, and thereafter heated under post-curing conditions (at 220 to 350°C for 10 to 6,000 minutes) to prepare the cured product by a post-curing reaction. Subsequently, after the above cured product is allowed to stand at 250°C for 1,000 hours, the weight thereof is measured, and the rate of the weight loss thereof is calculated.

[0035] The production method of the invention includes blending and mixing the allyletherified phenol resin (ingredient (A)), the epoxy resin (ingredient (B)) and the curing accelerator (ingredient (C)) so as to become predetermined contents, then, first heating the resulting composition at a temperature of 100 to 200°C for 1 to 60 minutes, and thereafter, further heating it at a temperature of 220 to 350°C for 10 to 6,000 minutes, thereby curing the thermosetting resin composition to prepare the cured product.

[0036] The cured product obtained by the production method of the invention is particularly excellent in heat resistance, so that it is suitably used, for example, in electronic materials such as electronic parts, laminates for printed-wiring boards and printed-wiring boards, semiconductor encapsulating materials and semiconductor-mounted modules, automobiles and vehicles, aircraft parts, building components, machine tools and the like.

EXAMPLES

[0037] Examples of the invention will be described below together with Comparative Examples. However, the invention should not be construed as being limited to these Examples. Incidentally, "parts" and "%" in Examples are defined as "parts by weight" and "% by weight" respectively, unless otherwise specified.

[0038] First, prior to the preparation of thermosetting resin compositions, partially allyletherified phenol resins were synthesized (Synthesis Examples A-1 to A-4).

[Synthesis Example A-1]

[0039] A phenol resin (GS-180, manufactured by Gunei Chemical Industry Co., Ltd., phenol equivalent: 105 g/eq.) (105 parts), 90.7 parts of allyl bromide (manufactured by Tokyo Chemical Industry Co., Ltd.), 138.2 parts of potassium carbonate (manufactured by Wako Pure Chemical Industries, Ltd.) and 500 parts of acetone (manufactured by Wako Pure Chemical Industries, Ltd.) were mixed, and refluxed under heating for 24 hours in a nitrogen gas stream. After cooling to room temperature (25°C), filtration and concentration were performed, and 400 parts of ethyl acetate (manufactured by Wako Pure Chemical Industries, Ltd.) was added to a residue, followed by washing once with 200 parts of a 5% solution of hydrochloric acid (manufactured by Wako Pure Chemical Industries, Ltd.) diluted with distilled water and washing twice with 200-part portions of distilled water. Thereafter, an organic layer was extracted and dried with magnesium sulfate (manufactured by Wako Pure Chemical Industries, Ltd.), followed by filtration and concentration to obtain a desired partially allyletherified phenol resin (APN-1) having the above structural units (1) and (2) and having an allylation ratio of 64.9%.

[Synthesis Example A-2]

[0040] A phenol resin (GS-180, manufactured by Gunei Chemical Industry Co., Ltd., phenol equivalent: 105 g/eq.) (105 parts), 60.5 parts of allyl bromide (manufactured by Tokyo Chemical Industry Co., Ltd.), 103.7 parts of potassium carbonate (manufactured by Wako Pure Chemical Industries, Ltd.) and 500 parts of acetone (manufactured by Wako Pure Chemical Industries, Ltd.) were mixed, and refluxed under heating for 24 hours in a nitrogen gas stream. After cooling to room temperature (25°C), filtration and concentration were performed, and 400 parts of ethyl acetate (man-

ufactured by Wako Pure Chemical Industries, Ltd.) was added to a residue, followed by washing once with 200 parts of a 5% solution of hydrochloric acid (manufactured by Wako Pure Chemical Industries, Ltd.) diluted with distilled water and washing twice with 200-part portions of distilled water. Thereafter, an organic layer was extracted and dried with magnesium sulfate (manufactured by Wako Pure Chemical Industries, Ltd.), followed by filtration and concentration to obtain a desired partially allyletherified phenol resin (APN-2) having the above structural units (1) and (2) and having an allylation ratio of 43.3%.

[Synthesis Example A-3]

[0041] A phenol resin (GS-180, manufactured by Gunei Chemical Industry Co., Ltd., phenol equivalent: 105 g/eq.) (105 parts), 30.3 parts of allyl bromide (manufactured by Tokyo Chemical Industry Co., Ltd.), 69.1 parts of potassium carbonate (manufactured by Wako Pure Chemical Industries, Ltd.) and 500 parts of acetone (manufactured by Wako Pure Chemical Industries, Ltd.) were mixed, and refluxed under heating for 24 hours in a nitrogen gas stream. After cooling to room temperature (25°C), filtration and concentration were performed, and 400 parts of ethyl acetate (manufactured by Wako Pure Chemical Industries, Ltd.) was added to a residue, followed by washing once with 200 parts of a 5% solution of hydrochloric acid (manufactured by Wako Pure Chemical Industries, Ltd.) diluted with distilled water and washing twice with 200-part portions of distilled water. Thereafter, an organic layer was extracted and dried with magnesium sulfate (manufactured by Wako Pure Chemical Industries, Ltd.), followed by filtration and concentration to obtain a desired partially allyletherified phenol resin (APN-3) having the above structural units (1) and (2) and having an allylation ratio of 21.5%.

[Synthesis Example A-4]

[0042] A phenol resin (GS-180, manufactured by Gunei Chemical Industry Co., Ltd., phenol equivalent: 105 g/eq.) (105 parts), 12.1 parts of allyl bromide (manufactured by Tokyo Chemical Industry Co., Ltd.), 34.6 parts of potassium carbonate (manufactured by Wako Pure Chemical Industries, Ltd.) and 500 parts of acetone (manufactured by Wako Pure Chemical Industries, Ltd.) were mixed, and refluxed under heating for 24 hours in a nitrogen gas stream. After cooling to room temperature (25°C), filtration and concentration were performed, and 400 parts of ethyl acetate (manufactured by Wako Pure Chemical Industries, Ltd.) was added to a residue, followed by washing once with 200 parts of a 5% solution of hydrochloric acid (manufactured by Wako Pure Chemical Industries, Ltd.) diluted with distilled water and washing twice with 200-part portions of distilled water. Thereafter, an organic layer was extracted and dried with magnesium sulfate (manufactured by Wako Pure Chemical Industries, Ltd.), followed by filtration and concentration to obtain a desired partially allyletherified phenol resin (APN-4) having the above structural units (1) and (2) and having an allylation ratio of 9.5%.

[0043] On the other hand, respective ingredients shown below were prepared.

[Epoxy Resin B1]

[0044] EPPN-501HY (epoxy equivalent: 169 g/eq., manufactured by Nippon Kayaku Co., Ltd.)

[Epoxy Resin B2]

[0045] KI-3000 (epoxy equivalent: 200 g/eq., manufactured by Tohto Kasei Co., Ltd.)

[Curing Accelerator]

[0046] TPP (triphenylphosphine, manufactured by Tokyo Chemical Industry Co., Ltd.)

[Examples 1 to 24]

[0047] Using the partially allyletherified phenol resins (APN-1, APN-2, APN-3 and APN-4) obtained in the above Synthesis Examples A-1 to A-4 as phenol resins, the epoxy resin B1 and the curing accelerator (triphenylphosphine), thermosetting resin compositions were prepared by blending and mixing them in the compounding ratios shown in Tables 1 to 6 given later. Then, the above thermosetting resin compositions were cured by heating at 175°C for 5 minutes, and thereafter, further heated under the post-curing conditions (predetermined temperature and predetermined time) shown in Tables 1 to 6 given later to perform post-curing, thereby preparing cured products of the thermosetting resin compositions.

[0048] Using the partially allyletherified phenol resins (APN-1, APN-2, APN-3 and APN-4) obtained in the above

Synthesis Examples A-1 to A-4 as phenol resins, the epoxy resin B2 and the curing accelerator (triphenylphosphine), thermosetting resin compositions were prepared by blending and mixing them in the compounding ratios shown in Tables 7 to 9 given later. Then, the above thermosetting resin compositions were cured by heating at 175°C for 5 minutes, and thereafter, further heated under the post-curing conditions (predetermined temperature and predetermined time) shown in Tables 7 to 9 given later to perform post-curing, thereby preparing cured products of the thermosetting resin compositions.

[Comparative Examples 1 to 5]

[0049] Using the allyl group-free phenol resin (GS-180, phenolic hydroxyl group equivalent: 105 g/eq., manufactured by Gunei Chemical Industry Co., Ltd.) as a phenol resin, the epoxy resin B1 and the curing accelerator (triphenylphosphine), thermosetting resin compositions were prepared by blending and mixing them in the compounding ratios shown in Table 10 given later. Then, the above thermosetting resin compositions were cured by heating at 175°C for 5 minutes, and thereafter, further heated under the post-curing conditions (predetermined temperature and predetermined time) shown in Table 10 given later to perform post-curing, thereby preparing cured products of the thermosetting resin compositions.

[Comparative Examples 6 to 10]

[0050] Using the allyl group-free phenol resin (GS-180, phenolic hydroxyl group equivalent: 105 g/eq., manufactured by Gunei Chemical Industry Co., Ltd.) as a phenol resin, the epoxy resin B2 and the curing accelerator (triphenylphosphine), thermosetting resin compositions were prepared by blending and mixing them in the compounding ratios shown in Table 11 given later. Then, the above thermosetting resin compositions were cured by heating at 175°C for 5 minutes, and thereafter, further heated under the post-curing conditions (predetermined temperature and predetermined time) shown in Table 11 given later to perform post-curing, thereby preparing cured products of the thermosetting resin compositions.

[Comparative Examples 11 to 26]

[0051] Using the partially allyletherified phenol resins (APN-1, APN-2, APN-3 and APN-4) obtained in the above Synthesis Examples A-1 to A-4 as phenol resins, the epoxy resin B1 and the curing accelerator (triphenylphosphine), thermosetting resin compositions were prepared by blending and mixing them in the compounding ratios shown in Tables 12 to 15 given later. Then, the above thermosetting resin compositions were cured by heating at 175°C for 5 minutes, and thereafter, further heated under the post-curing conditions (predetermined temperature and predetermined time) shown in Tables 12 to 15 given later to perform post-curing, thereby preparing cured products of the thermosetting resin compositions.

[Comparative Examples 27 to 34]

[0052] Using the partially allyletherified phenol resins (APN-1, APN-2, APN-3 and APN-4) obtained in the above Synthesis Examples A-1 to A-4 as phenol resins, the epoxy resin B2 and the curing accelerator (triphenylphosphine), thermosetting resin compositions were prepared by blending and mixing them in the compounding ratios shown in Tables 16 and 17 given later. Then, the above thermosetting resin compositions were cured by heating at 175°C for 5 minutes, and thereafter, further heated under the post-curing conditions (predetermined temperature and predetermined time) shown in Tables 16 and 17 given later to perform post-curing, thereby preparing cured products of the thermosetting resin compositions.

[0053] Using the thermosetting resin compositions thus obtained and the cured products thereof, characteristics (glass transition temperature, dynamic viscoelasticity and long-term heat resistance) were measured and evaluated by the following methods. The results thereof are also shown in Tables 1 to 17 given later.

[Long-Term Heat Resistance]

[0054] About 2 g of each of the above thermosetting resin compositions was put in an aluminum cup, and the resin composition sample put in the aluminum cup was placed on a hot plate set to 175°C, followed by curing by heating for 5 minutes. Thereafter, the sample was heated under the post-curing conditions (predetermined temperature and predetermined time) shown in Tables 1 to 17 to perform post-curing. The cured product sample which underwent the above series of curing processes was put in a hot-air oven set to 250°C, and 1,000-hour long-term heat resistance was evaluated according to the following criteria:

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Excellent: the weight loss ratio at 250°C for 1,000 hours was 5% or less.

Good: the weight loss ratio at 250°C for 1,000 hours was from more than 5% to 7.5%.

Fair: the weight loss ratio at 250°C for 1,000 hours was from more than 7.5% to 10%.

Poor: the weight loss ratio at 250°C for 1,000 hours was more than 10%.

5

[Glass Transition Temperature]

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[0055] Cured product samples (2 mm in thickness, 5 mm in width and 20 mm in length) were prepared under the same conditions (curing by heating at 175°C for 5 minutes and the post-curing conditions shown in Tables 1 to 17) as in the above long-term heat resistance evaluation, and the glass transition temperature was measured using a dynamic viscoelasticity measuring device (manufactured by SII Nano Technology Inc.). From the data obtained, the temperature at the maximum peak value of tanD was taken as the glass transition temperature (°C).

15

[Dynamic Viscoelasticity]

20

[0056] Cured product samples (2 mm in thickness, 5 mm in width and 20 mm in length) were prepared under the same conditions (curing by heating at 175°C for 5 minutes and the post-curing conditions shown in Tables 1 to 17) as in the above long-term heat resistance evaluation, and the glass transition temperature was measured using a dynamic viscoelasticity measuring device (manufactured by SII Nano Technology Inc.). From the data obtained, the values of the storage elastic modulus (E') at 25°C and 200°C were taken as the dynamic viscoelasticity at the respective temperatures.

[0057]

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Table 1

[Use Example of Epoxy Resin B1]

(parts)

	Example			
	1	2	3	4
Partially Allyletherified Phenol Resin	50 (APN-1)	50 (APN-2)	50 (APN-3)	50 (APN-4)
Epoxy Resin B1	50	50	50	50
Curing Accelerator (TPP)	1	1	1	1
Allylation ratio (%)	64.9	43.3	21.5	9.5
Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
Epoxy Number (g/eq.)	169	169	169	169
Epoxy equivalent/ Phenolic hydroxyl group equivalent	2.21	1.28	0.86	0.71
Post-Curing Conditions*	E	E	E	E
Glass Transition Temperature (°C)	255	242	218	206
Dynamic Viscoelasticity (MPa)	25°C	2950	3230	3010
	200°C	1500	1410	863
Long-Term Heat Resistance	Excellent	Excellent	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0058]

Table 2

[Use Example of Epoxy Resin B1]

(parts)

		Example			
		5	6	7	8
	Partially Allyletherified Phenol Resin	50 (APN-1)	50 (APN-2)	50 (APN-3)	50 (APN-4)
	Epoxy Resin B1	50	50	50	50
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	169	169	169	169
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	2.21	1.28	0.86	0.71
	Post-Curing Conditions*	D	D	D	D
	Glass Transition Temperature (°C)	215	226	227	205
	Dynamic Viscoelasticity (MPa)	25°C	3520	3400	3330
		200°C	1170	1280	1180
	Long-Term Heat Resistance	Excellent	Excellent	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0059]

Table 3

[Use Example of Epoxy Resin B1]

(parts)

	Example			
	9	10	11	12
Partially Allyletherified Phenol Resin	50 (APN-1)	50 (APN-2)	50 (APN-3)	50 (APN-4)
Epoxy Resin B1	50	50	50	50
Curing Accelerator (TPP)	1	1	1	1
Allylation ratio (%)	64.9	43.3	21.5	9.5
Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
Epoxy Number (g/eq.)	169	169	169	169
Epoxy equivalent/ Phenolic hydroxyl group equivalent	2.21	1.28	0.86	0.71
Post-Curing Conditions*	C	C	C	C
Glass Transition Temperature (°C)	177	173	182	180
Dynamic Viscoelasticity (MPa)	25°C	3350	3220	2970
	200°C	256	349	476
Long-Term Heat Resistance	Excellent	Excellent	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0060]

Table 4

[Use Example of Epoxy Resin B1]

(parts)

		Example			
		13	14	15	16
	Partially Allyletherified Phenol Resin	68.8 (APN-1)	56.1 (APN-2)	46.1 (APN-3)	41.6 (APN-4)
	Epoxy Resin B1	31.2	43.9	53.9	58.4
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	169	169	169	169
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	E	E	E	E
	Glass Transition Temperature (°C)	240	226	208	180
	Dynamic Viscoelasticity (MPa)	25°C	3320	3020	3460
		200°C	1580	1410	465
	Long-Term Heat Resistance	Excellent	Excellent	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0061]

Table 5

[Use Example of Epoxy Resin B1]

(parts)

		Example			
		17	18	19	20
	Partially Allyletherified Phenol Resin	68.8 (APN-1)	56.1 (APN-2)	46.1 (APN-3)	41.6 (APN-4)
	Epoxy Resin B1	31.2	43.9	53.9	58.4
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	169	169	169	169
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	D	D	D	D
	Glass Transition Temperature (°C)	223	211	199	181
	Dynamic Viscoelasticity (MPa)	25°C	4160	3290	3040
		200°C	160	258	162
	Long-Term Heat Resistance	Excellent	Excellent	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0062]

Table 6

[Use Example of Epoxy Resin B1]

(parts)

		Example			
		21	22	23	24
	Partially Allyletherified Phenol Resin	68.8 (APN-1)	56.1 (APN-2)	46.1 (APN-3)	41.6 (APN-4)
	Epoxy Resin B1	31.2	43.9	53.9	58.4
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	169	169	169	169
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	C	C	C	C
	Glass Transition Temperature (°C)	181	188	173	175
	Dynamic Viscoelasticity (MPa)	25°C	2760	2600	3140
		200°C	218	249	192
	Long-Term Heat Resistance	Excellent	Good	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0063]

Table 7

[Use Example of Epoxy Resin B2]

(parts)

	Example			
	25	26	27	28
Partially Allyletherified Phenol Resin	65.1 (APN-1)	51.9 (APN-2)	42.0 (APN-3)	37.5 (APN-4)
Epoxy Resin B2	34.9	48.1	58.0	62.5
Curing Accelerator (TPP)	1	1	1	1
Allylation ratio (%)	64.9	43.3	21.5	9.5
Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
Epoxy Number (g/eq.)	200	200	200	200
Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
Post-Curing Conditions*	E	E	E	E
Glass Transition Temperature (°C)	219	194	196	184
Dynamic Viscoelasticity (MPa)	25°C	3930	1390	3420
	200°C	1260	278	139
Long-Term Heat Resistance	Excellent	Excellent	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0064]

Table 8

[Use Example of Epoxy Resin B2]

(parts)

		Example			
		29	30	31	32
	Partially Allyletherified Phenol Resin	65.1 (APN-1)	51.9 (APN-2)	42.0 (APN-3)	37.5 (APN-4)
	Epoxy Resin B2	34.9	48.1	58.0	62.5
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	200	200	200	200
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	D	D	D	D
	Glass Transition Temperature (°C)	201	198	204	185
	Dynamic Viscoelasticity (MPa)	25°C	3270	3250	2900
		200°C	146	330	488
	Long-Term Heat Resistance	Excellent	Excellent	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0065]

Table 9

[Use Example of Epoxy Resin B2]

(parts)

	Example			
	33	34	35	36
Partially Allyletherified Phenol Resin	65.1 (APN-1)	51.9 (APN-2)	42.0 (APN-3)	37.5 (APN-4)
Epoxy Resin B2	34.9	48.1	58.0	62.5
Curing Accelerator (TPP)	1	1	1	1
Allylation ratio (%)	64.9	43.3	21.5	9.5
Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
Epoxy Number (g/eq.)	200	200	200	200
Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
Post-Curing Conditions*	C	C	C	C
Glass Transition Temperature (°C)	175	183	186	173
Dynamic Viscoelasticity (MPa)	25°C	3800	3110	3640
	200°C	137	158	173
Long-Term Heat Resistance	Good	Good	Good	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0066]

Table 10

[Use Example of Epoxy Resin B1]

(parts)

		Comparative Example				
		1	2	3	4	5
Phenol Resin		50 (GS-180)	50 (GS-180)	50 (GS-180)	50 (GS-180)	50 (GS-180)
Epoxy Resin B1		50	50	50	50	50
Curing Accelerator (TPP)		1	1	1	1	1
Allylation ratio (%)		0	0	0	0	0
Phenol Number (g/eq.)		105	105	105	105	105
Allyl Number (g/eq.)		0	0	0	0	0
Epoxy Number (g/eq.)		169	169	169	169	169
Epoxy equivalent/ Phenolic hydroxyl group equivalent		0.62	0.62	0.62	0.62	0.62
Post-Curing Conditions*		A	B	C	D	E
Glass Transition Temperature (°C)		158	161	167	162	157
Dynamic Viscoelasticity (MPa)	25°C	3010	3690	3480	2870	3150
	200°C	36	98	87	147	143
Long-Term Heat Resistance		Poor	Poor	Poor	Poor	Poor

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0067]

Table 11

[Use Example of Epoxy Resin B2]

(parts)

		Comparative Example				
		6	7	8	9	10
	Phenol Resin	34.4 (GS-180)	34.4 (GS-180)	34.4 (GS-180)	34.4 (GS-180)	34.4 (GS-180)
	Epoxy Resin B2	65.6	65.6	65.6	65.6	65.6
	Curing Accelerator (TPP)	1	1	1	1	1
	Allylation ratio (%)	0	0	0	0	0
	Phenol Number (g/eq.)	105	105	105	105	105
	Allyl Number (g/eq.)	0	0	0	0	0
	Epoxy Number (g/eq.)	200	200	200	200	200
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	A	B	C	D	E
	Glass Transition Temperature (°C)	162	169	162	169	157
	Dynamic Viscoelasticity (MPa)	25°C	2650	2150	2690	2280
		200°C	55	73	68	102
	Long-Term Heat Resistance	Poor	Poor	Poor	Poor	Poor

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0068]

Table 12

[Use Example of Epoxy Resin B1]

(parts)

		Comparative Example			
		11	12	13	14
	Partially Allyletherified Phenol Resin	50 (APN-1)	50 (APN-2)	50 (APN-3)	50 (APN-4)
	Epoxy Resin B1	50	50	50	50
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	169	169	169	169
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	2.21	1.28	0.86	0.71
	Post-Curing Conditions*	A	A	A	A
	Glass Transition Temperature (°C)	41	67	167	164
	Dynamic Viscoelasticity (MPa)	25°C	51	2920	3160
		200°C	-	136	208
	Long-Term Heat Resistance	Fair	Fair	Poor	Poor

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0069]

Table 13

[Use Example of Epoxy Resin B1]

(parts)

	Comparative Example			
	15	16	17	18
Partially Allyletherified Phenol Resin	50 (APN-1)	50 (APN-2)	50 (APN-3)	50 (APN-4)
Epoxy Resin B1	50	50	50	50
Curing Accelerator (TPP)	1	1	1	1
Allylation ratio (%)	64.9	43.3	21.5	9.5
Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
Epoxy Number (g/eq.)	169	169	169	169
Epoxy equivalent/ Phenolic hydroxyl group equivalent	2.21	1.28	0.86	0.71
Post-Curing Conditions*	B	B	B	B
Glass Transition Temperature (°C)	82	117	163	165
Dynamic Viscoelasticity (MPa)	25°C	2560	3200	2950
	200°C	33	89	234
Long-Term Heat Resistance	Good	Good	Fair	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0070]

Table 14

[Use Example of Epoxy Resin B1]

(parts)

		Comparative Example			
		19	20	21	22
	Partially Allyletherified Phenol Resin	68.8 (APN-1)	56.1 (APN-2)	46.1 (APN-3)	41.6 (APN-4)
	Epoxy Resin B1	31.2	43.9	53.9	58.4
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	169	169	169	169
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	A	A	A	A
	Glass Transition Temperature (°C)	39	66	159	161
	Dynamic Viscoelasticity (MPa)	25°C	786	3230	3420
		200°C	5	20	139
	Long-Term Heat Resistance	Fair	Fair	Poor	Poor

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0071]

Table 15

[Use Example of Epoxy Resin B1]

(parts)

		Comparative Example			
		23	24	25	26
	Partially Allyletherified Phenol Resin	68.8 (APN-1)	56.1 (APN-2)	46.1 (APN-3)	41.6 (APN-4)
	Epoxy Resin B1	31.2	43.9	53.9	58.4
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	169	169	169	169
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	B	B	B	B
	Glass Transition Temperature (°C)	62	95	164	168
	Dynamic Viscoelasticity (MPa)	25°C	3510	2800	3360
		200°C	65	72	128
	Long-Term Heat Resistance	Good	Good	Fair	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0072]

Table 16

[Use Example of Epoxy Resin B2]

(parts)

		Comparative Example			
		27	28	29	30
	Partially Allyletherified Phenol Resin	65.1 (APN-1)	51.9 (APN-2)	42.0 (APN-3)	37.5 (APN-4)
	Epoxy Resin B2	34.9	48.1	58.0	62.5
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	200	200	200	200
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	A	A	A	A
	Glass Transition Temperature (°C)	39	66	131	161
	Dynamic Viscoelasticity (MPa)	25°C	786	1390	2820
		200°C	5.1	20	72
	Long-Term Heat Resistance	Fair	Poor	Poor	Poor

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0073]

Table 17

[Use Example of Epoxy Resin B2]

(parts)

		Comparative Example			
		31	32	33	34
	Partially Allyletherified Phenol Resin	65.1 (APN-1)	51.9 (APN-2)	42.0 (APN-3)	37.5 (APN-4)
	Epoxy Resin B2	34.9	48.1	58.0	62.5
	Curing Accelerator (TPP)	1	1	1	1
	Allylation ratio (%)	64.9	43.3	21.5	9.5
	Phenol Number (g/eq.)	373.1	215.7	144.7	120.2
	Allyl Number (g/eq.)	201.8	282.5	528.4	1145.3
	Epoxy Number (g/eq.)	200	200	200	200
	Epoxy equivalent/ Phenolic hydroxyl group equivalent	1.00	1.00	1.00	1.00
	Post-Curing Conditions*	B	B	B	B
	Glass Transition Temperature (°C)	53	90	159	161
	Dynamic Viscoelasticity (MPa)	25°C	3860	3830	3550
		200°C	20	37	162
	Long-Term Heat Resistance	Good	Good	Fair	Fair

* A: at 175°C for 10 hours

B: at 200°C for 100 hours

C: at 220°C for 100 hours

D: at 250°C for 10 hours

E: at 300°C for 5 hours

[0074] The above results show that the samples of Examples as the cured products prepared using the allyletherified phenol resin under the specific curing reaction conditions have high glass transition temperature and high dynamic viscoelasticity (25°C and 200°C). Also with regard to long-term heat resistance, the good results are obtained.

[0075] On the other hand, the samples of Comparative Examples 1 to 10 as the cured products prepared using the ordinary phenol resin having no allyl group have low glass transition temperature and low dynamic viscoelasticity at 200°C. Moreover, in the evaluation of long-term heat resistance, they have high weight loss ratio, leading to the poor evaluation results with regard to long-term heat resistance.

[0076] Further, all the samples of Comparative Examples 11 to 34 as the cured products prepared under the conditions departing from the specific curing reaction conditions have low glass transition temperature and low dynamic viscoelasticity at 200°C, similarly to the samples of Comparative Examples described above. Moreover, in the evaluation of long-term heat resistance, the poor evaluation results are obtained with regard to long-term heat resistance, compared to the samples of Examples, although the weight loss ratio is confirmed to be depressed in some cases, compared to the samples of Comparative Examples 1 to 10.

[0077] Then, there were measured changes in glass transition temperature of the cured products depending on the post-curing conditions at the time when the cured products were prepared (at 175°C for 5 minutes + post-curing) using

the allyletherified phenol resins (APN-1 to APN-4) and the phenol resin (GS-180) and the epoxy resin B1 (EPPN-501HY) at a compounding molar ratio of 50/50. The results thereof are shown in Fig. 1. Further, there were measured changes in glass transition temperature of the cured products depending on the post-curing conditions at the time when the cured products were prepared (at 175°C for 5 minutes + post-curing) using the allyletherified phenol resins (APN-1 to APN-4) and the phenol resin (GS-180) and the epoxy resin B2 (KI-3000) at a compounding molar ratio of 50/50. The results thereof are shown in Fig. 2. That is to say, Fig. 1 and Fig. 2 are graphs showing the changes in glass transition temperature of the cured products depending on the difference in the post-curing conditions, when curing was performed at 175°C for 5 minutes. Incidentally, the glass transition temperature was measured in the same manner as described above. The results show that in the case where the allyletherified phenol resins are used, the glass transition temperature significantly increases in a high-temperature region of the post-curing temperature, particularly in a high-temperature region exceeding 220°C, to provide the cured products having a glass transition temperature exceeding 200°C, even when the epoxy resin has a common skeleton. As contrasted therewith, the results show that in the case where the phenol resin not allyletherified (GS-180) is used, the glass transition temperature is approximately constant regardless of the post-curing conditions.

[0078] While the invention has been described in detail with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Incidentally, the present application is based on Japanese Patent Application No. 2010-156235 filed on July 8, 2010, and the contents are incorporated herein by reference.

All references cited herein are incorporated by reference herein in their entirety. Also, all the references cited herein are incorporated as a whole.

[0079] The cured product obtained by the method for producing a cured product of a thermosetting resin composition according to the invention has excellent long-term heat resistance and high glass transition temperature which can not be realized by the conventional thermosetting resin compositions, and is useful as a heat-resistant-insulating resin for electronic materials. Specifically, the electronic materials include, for example, electronic parts, laminates for printed-wiring boards and printed-wiring boards, semiconductor encapsulating materials, semiconductor-mounted modules and the like. Further, it is also suitably used in automobiles and vehicles, aircraft parts, building components, machine tools and the like.

Claims

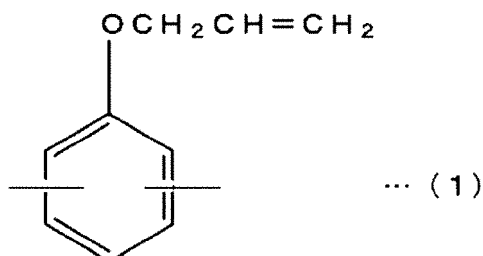
1. A method for producing a cured product of a thermosetting resin composition, said method comprising: heating a thermosetting resin composition comprising the following ingredients (A) to (C) at a temperature of 100 to 200°C for 1 to 60 minutes; and then further heating the thermosetting resin composition at a temperature of 220 to 350°C for 10 to 6,000 minutes, thereby curing the thermosetting resin composition:

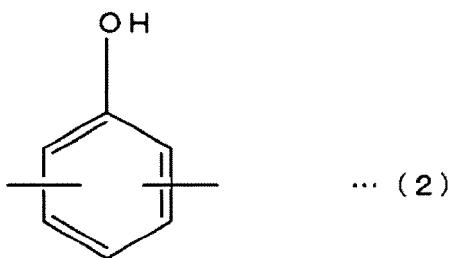
(A) an allyletherified phenol resin;

(B) an epoxy resin; and

(C) a curing accelerator.

2. The method for producing a cured product of a thermosetting resin composition according to claim 1, wherein the allyletherified phenol resin as ingredient (A) contains the following structural units (1) and (2):





- 15
3. The method for producing a cured product of a thermosetting resin composition according to claim 1 or 2, wherein the allyletherified phenol resin as ingredient (A) has an allyl group equivalent of 100 to 3,000 (g/eq.).
- 20
4. The method for producing a cured product of a thermosetting resin composition according to any one of claims 1 to 3, wherein the allyletherified phenol resin as ingredient (A) has a phenolic hydroxyl group equivalent of 100 to 3,000 (g/eq.).
- 25
5. A cured product obtained by the method for producing a cured product of a thermosetting resin composition according to any one of claims 1 to 4.
- 30
- 35
- 40
- 45
- 50
- 55

Fig. 1

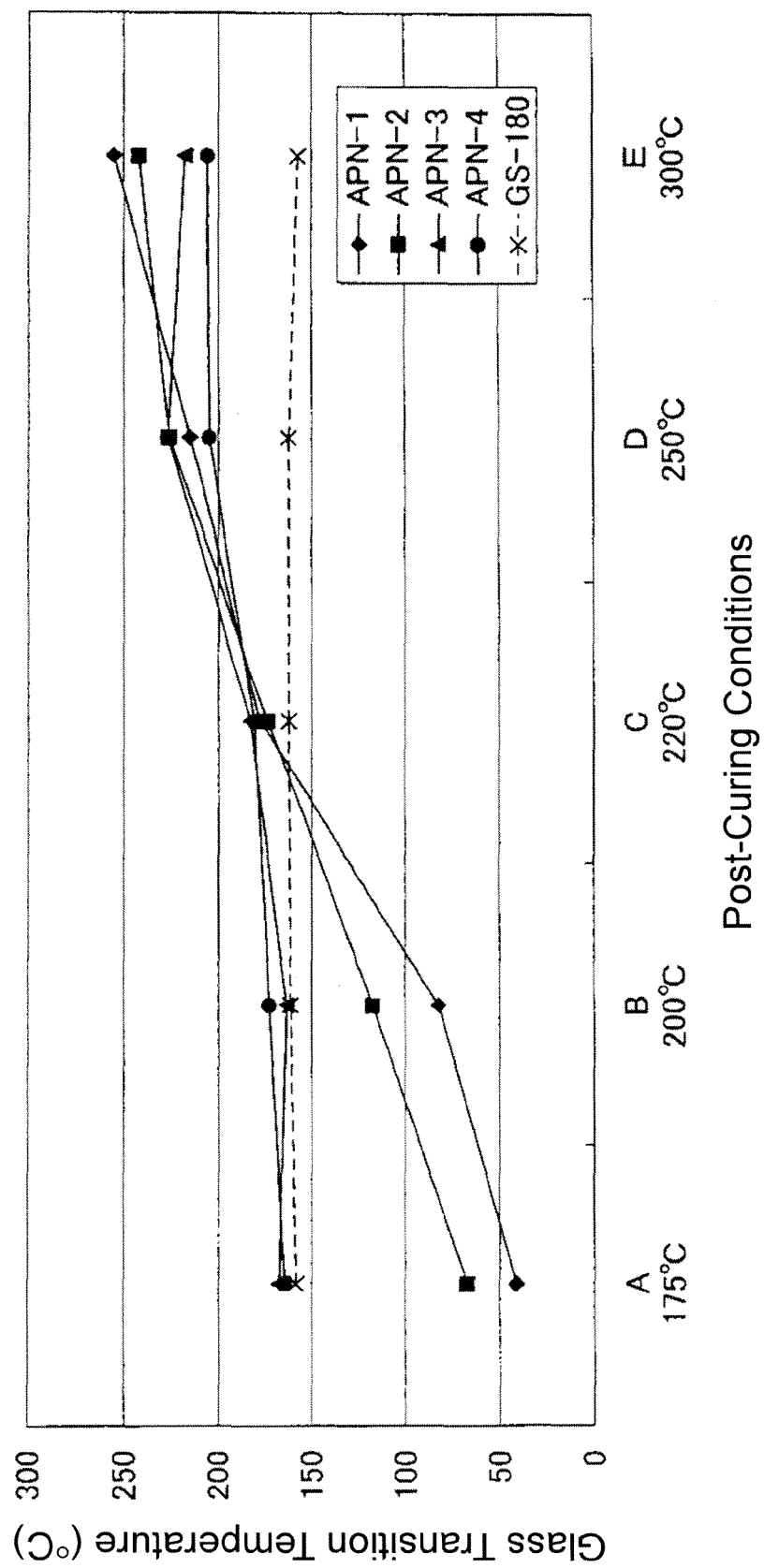
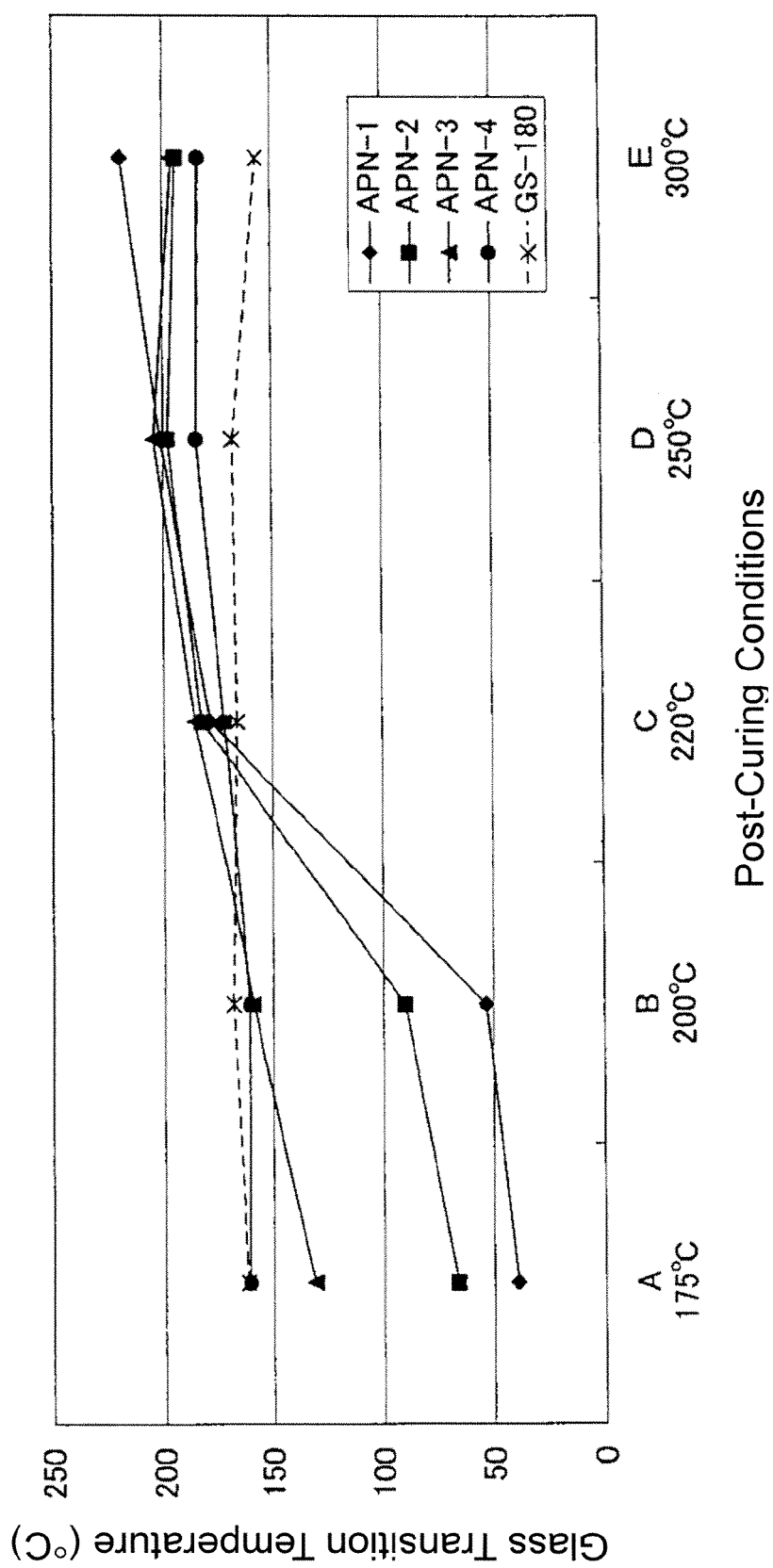


Fig. 2





EUROPEAN SEARCH REPORT

Application Number
EP 11 17 3032

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			C08G C08L C08J
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 28 September 2011	Examiner Friebe, Lars
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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